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Growth and nanostructure of tellurides for optoelectronic, thermoelectric and phase-change applications

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Chapter 1. Introduction – Why study tellurides?



Crystal structures, open questions and applications of bulk and thin-film tellurides are discussed. The quest for artificial nanostructuring in thin films is introduced. Finally, an outline of the thesis is given.

1.1 Why?

Any question of ‘why’ may be asked and answered on several levels. This chapter will attempt to answer the titular question in a few more and less profound ways. Obviously we describe the wide range of promising applications of tellurides, which may positively affect the people and world we live in. We introduce some mysteries any curious scientist would like to start solving immediately. We also show the fascinating structures they form, as well as synthesis equipment allowing us to play with their building blocks and satisfy our inner child. These answers however, while valid and true, seem less appropriate than the answer George Mallory gave in 1923, when asked why he would lead an expedition up the thus far unclimbed Mount Everest: “Because it’s there”.

1.2 Crystal Structure and epitaxy

The crystal structure of the group V_2-VI_3 tellurides (e.g. Bi_2Te_3) is highly anisotropic, as can be seen in figure 1. In fact, while the bonding within a so-called quintuple-layer block ($|Te-Bi-Te-Bi-Te|$) is relatively strong since it is based on covalent bonds adjacent Te layers are only weakly bound by molecular or van der Waals (vdW) forces. Recently it has been argued that these tellurides contain a special type of bonding called ‘metavalent’.¹ Although not as anisotropic as V_2-VI_3 materials, IV-VI materials (e.g. $GeTe$) tend towards a Peierls-like distortion from the rocksalt structure which gives rise to the formation of IV-VI bilayers ($|Ge-Te|$) along the hexagonal $[0001]$ (rhombohedral/cubic $[111]$) axis.² Furthermore, due to the thermodynamically favourable mixing and identical (0001) surface symmetry of $GeTe$ and Sb_2Te_3/Bi_2Te_3 , $IV_x-V_{2y}-VI_{x+1.5y}$ structures containing vdW gaps can be grown, of which, as an example, $Ge_2Sb_2Te_5$ is depicted in the Kooi stacking in figure 1.^{3,4} These GST/GBT-materials are widely used in several technologies, which will be discussed in the following sections. All the above mentioned telluride crystals in their stable states belong to the trigonal crystal system and can be described by rhombohedral or hexagonal lattices.

Tungsten-telluride belong to a large class of materials called the Transition-Metal Di-Chalcogenides (TMDCs), which consist of triplet-layers $|Te-W-Te|$ separated by vdW gaps. Several structural modifications of WTe_2 may be stabilized, but when viewed along the 0001 (monoclinic 001) axis, all possess a (distorted) trigonal surface symmetry similar to that of the V_2-VI_3 materials. The use of crystalline TMDCs is currently mostly limited to fundamental research applications.

This anisotropy and weak interlayer bonding of these compounds is favourable for the synthesis, or growth of these ‘2D’ structures. Koma first introduced the concept of vdW epitaxy in 1991.⁵ Due to the weak interlayer bonding, he showed highly dissimilar materials could be stacked into a heterostructure with atomically sharp interfaces. Even more conveniently, the materials prefer to grow epitaxially, without generating lattice-matching strain. In 2014 Novoselov and Geim^{6,7} added to this idea by envisioning heterostructures of graphene, TMDCs and the aforementioned group V-VI materials to tune functional properties.^{6,7}

As we will show in this thesis, the concept of vdW epitaxy is a very useful one, allowing facile growth of heterostructures of various (quasi-)2D-bonded materials. This strong/weak bonding anisotropy also seems to give rise to several extremely useful functional properties, which we will discuss in the following sections.⁸

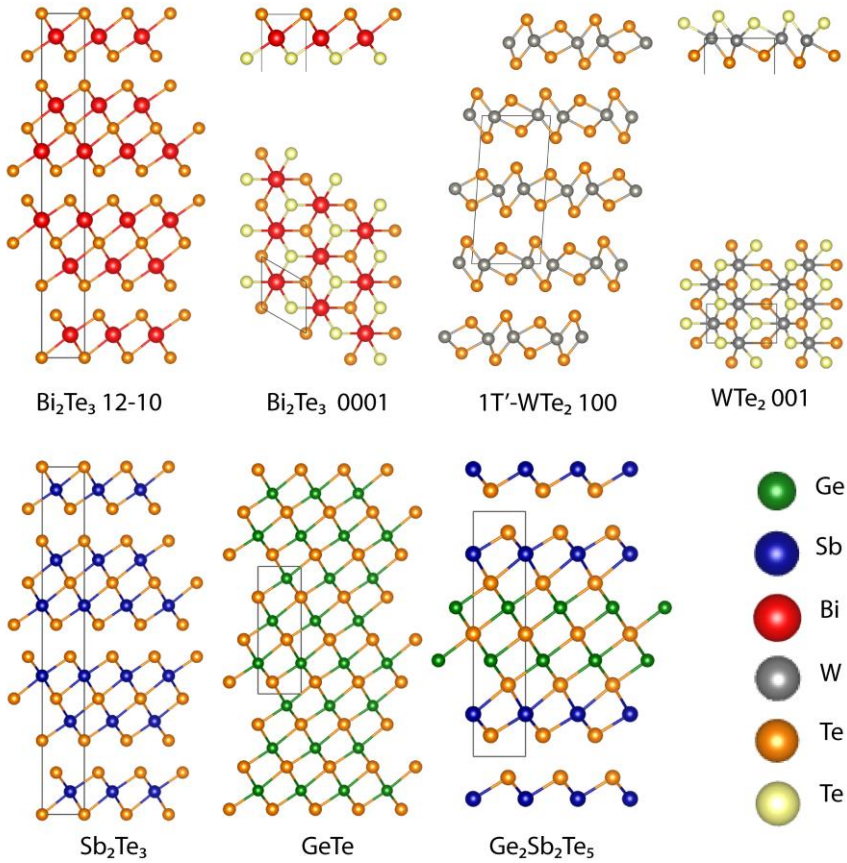


Figure 1. The crystal structures of several tellurides: Bi_2Te_3 , Sb_2Te_3 ($R\bar{3}m$), GeTe ($R3m$) and WTe_2 ($P2_1m$). While Bi_2Te_3 , Sb_2Te_3 and WTe_2 consist of quintuple or triplet layers separated by vdW gaps, a more subtle bond anisotropy is present in GeTe which causes alternatingly short and long Ge-Te bonds. This will generally lead to domain formation for films thicker than a few monolayers.⁹ The surfaces of all these tellurides can generally be treated as having hexagonal (sixfold) symmetry, which becomes apparent from the Bi_2Te_3 and WTe_2 structures viewed along the $[0001]$ crystal axis. The golden Te atoms reside at the vdW gap and form a hexagonally symmetric shape. Each Te atom is bound to three bismuth/tungsten-atoms however, reducing the symmetry to threefold. For $1\text{T}'\text{-WTe}_2$ the symmetry is further reduced by a distortion along the $[100]$ axis, creating alternating long- and short Te distances. GeTe and Sb_2Te_3 easily mix and form $\text{Ge}_2\text{Sb}_2\text{Te}_5$, here shown in the Kooi-structure,^{3,10} where the material forms nontuple blocks, with a preference for Sb to occupy the outer sites and Ge the inner sites.^{3,11,12}

1.3 Phase change materials

With the continuing exponential increase in data storage and computer memory requirements, ever smaller and more energy-efficient devices are needed. The GeSbTe alloys constitute the functional component in rewritable optical discs (CD, DVD, Blu-Ray).¹³ More recently they have been incorporated as on-chip memory elements which unlike some other popular memory elements, like DRAM and SRAM, persist after the power is removed.^{14,15} These cells have been manufactured to sizes around 50 nm, with their smallest dimension approaching several nanometers.^{16,17} The working principle of these memory cells, or bits, is equivalent in both optical and electrical applications. The phase-change material (PCM) is switched between a higher- and lower- electrically conducting or reflecting states, which represent the ‘0’ and ‘1’ bit states. This switch is accomplished using a melt-quench procedure. Using a weak light- (optical disk) or electric- (memory) heating pulse, the sample will switch from the amorphous to the crystalline phase. By applying a stronger pulse, the crystal film melts, and due to the high cooling rate within the cold surrounding, returns to the amorphous (glassy) state. The material can be cycled electrically about a billion times before degradation causes malfunction.¹⁸

The classical PCMs consisted of ‘bulk-like’ alloys. However using nanostructuring to engineer so-called interfacial phase-change materials (iPCM), it was shown that switching energy and time could be significantly reduced.¹⁹ These materials consist of a superlattice of epitaxially grown $\text{Ge}_2\text{Sb}_2\text{Te}_5$ and Sb_2Te_3 unit cell blocks, and seem to achieve both the high-and low resistance states within the crystalline phase. The exact nature of the switching mechanism and chemical bonding within these superlattices is still hotly debated.^{3,20}

It seems clear from many reports that engineering the exact texture and structure of a thin nanostructured film may provide tremendous improvement of functional properties. The use of a crystalline template to enhance crystallization rate,²¹ as well as the use of strained multilayers,^{22,23} where a GeTe layer is sandwiched between two Sb_2Te_3 layers, yield improved switching characteristics.

1.4 Thermoelectrics

The field of thermoelectrics (TEs) aims to optimize the Seebeck effect to harvest electrical current from heat gradients or, vice versa, using the Peltier effect to cool an area using electrical current.^{24,25} The energy-generating Seebeck effect has applications in any situation where regular power sources are unavailable, or no moving parts can be used, such as military or aerospace applications.²⁶ Waste heat sources such as steel manufacturing plants and solar arrays may also be sources of energy by using TE devices.²⁷ Peltier coolers may be applied for on-chip or in system cooling of small areas, where liquid or air-cooling cannot operate properly

or effectively.²⁸ While TE is an extremely large field, the Bi_2Te_3 and GeTe based TAGS (TeAgGeSb) families are among the most successful TE materials, and are still studied extensively.^{29,30}

The efficiency of a TE device is given by its figure of merit:

$$ZT = \frac{\sigma S^2}{\kappa} T \quad (1.1)$$

Where σ is the electrical conductivity, S the seebeck coefficient (in V/K) and κ the thermal conductivity in (W/mK).²⁵ The figure of merit immediately shows the dilemma of TE: optimum ZT is reached for a phonon glass (low κ) and electron crystal (high σ) or PGEC. In other words, one has to find a structure which conducts electrons extremely well, but blocks phonons (and high-energy electrons).²⁵ The Seebeck coefficient may be optimized by increasing the amount of additional electrons that become available when the temperature is increased: the Fermi level should be properly situated with respect to the band gap: a metal is therefore unfavorable.

As we discussed for PCMs, in TEs nanostructuring provides ways for improvement. Promising material systems are prepared using various dopants to improve the band structure, different heat-treatments are used to obtain various crystal structures and grain sizes in an attempt to reduce thermal conductivity.^{31,32} An early report on heterostructures of Sb_2Te_3 and Bi_2Te_3 claiming a strong reduction in κ was the inspiration for much more research into ordered multilayers continuing to this day.³³

The similarities between using tellurides for TEs and PCMs have been pointed out in the literature.³⁴ Both profit from low thermal conductivity (increasing energy efficiency), and both applications seem to show high performance when the materials involved possess a so-called metavalent bonding state, which can be broken by the thermal gradient or amorphisation pulse in the system.^{1,35} Furthermore, the expected lower thermal conductivity along the [0001] axis may be exploited in nanostructures and superlattices.

1.5 Optoelectronics

Bulk optical fibers

Optical sensor and communication fibers require the use of highly homogeneous bulk glassy materials. Traditionally selenium-based materials have been used due to the ease of obtaining the glassy state. More recently, attention has shifted to include the heavier tellurium which has a broader frequency transmission window but is harder to amorphise.^{36,37} Tellurium alloys can be alloyed with selenium without any phase segregation, as well as with arsenic, which

increases the glass forming ability. Although the optical and thermal properties of these alloys have been investigated frequently,³⁸ little is known concerning the actual microstructure and crystallization mechanism of these alloys, even in bulk.³⁹

Thin-film sensor and display

While phase-change optical disc storage constitutes a mature technology, and memory devices are industrially produced, active nanostructured optical systems such as displays and communication elements based on GST-like materials are still in the research phase. Due to the switchable nature of these materials, they are excellent candidates to be used as optical sensors, phase array antennas, display pixels, sub-wavelength optical lenses, and (anti-)reflective coatings. This requires development of tunable small-scale elements which possess high contrast, low noise, and are structurally stable under repeated switching.^{40–43}

TMDC-based optoelectronics

TMDC mono- or bilayers can show a variety of interesting behavior and properties: several of them are direct bandgap semiconductors, making them more suitable than graphene to use as transistors or sensors.^{44,45} They show high optical absorbance even at monolayer thickness, which is extremely suitable for incorporation within photovoltaic applications. This interaction is improved using graphene/TMDC heterostructures.^{46,47} Furthermore, the thin-film structure is stable against bending, and strain may even improve functional properties.⁴⁸ Major challenges include large-area deposition and long-term stability.

1.6 Pure nanoscale effects

Many nanometer scale research efforts, both theory and experimental work, focus on effects only observable in thin films approaching monolayer thickness. Topological Insulators (TI),^{49–51} Weyl semimetals,⁵² and effects like quantum spin-Hall effect,^{53,54} and superconductivity⁵⁵ are still poorly understood, but have been found for both the discussed group IV–VI and TMDC materials. Root cause of many of these effects is the discrepancy between electric potential at the material's edge and within the bulk: hence the need for extremely thin films or even monolayers. By isolating an extremely thin sample, edge states dominate properties. Especially for TMDCs, a strong discrepancy between mono- and bilayer films is reported due to a change in structure. Also for GeTe, a similar instability seems present.⁵⁶ The investigation of these effects and states requires extremely high-quality samples in terms of stoichiometry and thickness uniformity: these nanoscale phenomena rely on the absence of doping and concomitant impurity carriers. For this reason, the use of bulk or exfoliated crystals was usually preferred, but thin-film deposition techniques are rapidly improving.⁵⁷

1.7 Synthesis

All mentioned fields of application for tellurides require thin films to investigate nanoscale effects. As will become apparent in chapters two and three, this challenge is twofold: (1) one has to synthesize these films, and (2) then efficiently characterize them, neither of which is trivial at the nanoscale. For proper optimization, a quick back-and-forth interaction between both steps is essential.

The aim of this thesis was to grow telluride films using Pulsed Laser Deposition (PLD). While the technique is quite mature for the growth of oxides, other material classes have not been studied extensively. Specifically within the tellurides, the mature deposition methods include Molecular Beam Epitaxy (MBE) and sputtering. PLD promises to have several advantages over those techniques. Firstly, films generally adopt the target stoichiometry. Opposed to MBE, switching and adding ablation targets is much easier than exchanging or adding Knudsen cells. Furthermore, large-area PLD systems are already commercially available.⁵⁸ Finally, due to the PLD material versatility, targets can be oxide capped within the system. Compared to sputtering, the pulsed laser system and in-situ control through RHEED allow for more precise (monolayer) thickness control and diagnostics. The system therefore represents an ideal middle ground between control, accuracy, speed and versatility.

1.8 Summary

We have introduced the crystal structure of several telluride vdWals materials, which will feature in the following chapters. Furthermore, we shortly introduced the synthesis technique to make thin films. Several promising areas of investigation for telluride thin films, with a strong tie to functional applications have been introduced. These applications served as our guide in optimizing our thin film growth. Finally, we shortly outlined the deposition technique used to grow telluride thin films.

1.9 Outline of this thesis

The thesis can be divided into two parts: *artificial* nanostructures grown using PLD (chapters 3-6) and *natural* nanostructures (chapters 7-9).

Chapter 2 introduces the experimental techniques used in this thesis. Special attention is given to the pulsed laser deposition (PLD) technique and the attached reflective high-energy electron diffraction (RHEED) system.

Chapter 3 is devoted to experimental results concerning the growth of tellurides using PLD. The results mainly show the effect of varying different process parameters on the layer growth, and may be taken as a ‘tuning in’ of the system to optimum conditions.

Chapter 4 describes the growth optimization of WTe_2 using PLD. This challenging growth required single crystal targets and a thin seed layer of Bi_2Te_3 . We achieved low-temperature single-crystal-like growth of epitaxial heterostructures, and monolayer thickness control.

Chapter 5 elaborates on the growth of multilayered $(\text{Sb/Bi})_2\text{Te}_3 - \text{GeTe}$ films. Using RHEED we observed an unexpected and persistent long-range strain gradient within the films, which denies the paradigm of true vdWaals epitaxy.

Chapter 6 shows the optical properties of PLD grown films. We present multilayered devices which can be switched to obtain various reflectivity profiles.

Chapter 7 gives an analysis of the domain structures observed in GeTe and LaAlO_3 . They possess a similar crystallographic symmetry: a rhombohedrally distorted cubic structure. This gives rise to a herringbone domain structure, which alters the local crystal domain orientation, and might contribute to the high thermoelectric performance of GeTe. We proposed a crystallographic domain model for this herringbone structure, which is supported by TEM, EBSD, and optical microscopy, and is expected to be present in all structures based on a rhombohedral distortion of an initial cubic crystal structure.

Chapter 8 switches topics to the thermal analysis of reversible crystallization within the SeTe alloy system. We reveal an extended phase diagram for Se-Te as derived from Ultrafast Differential Scanning Calorimetry (UFDSC) analysis, and show that the alloys behave non-Arrhenian as a fragile (undercooled) liquid at high heating rates.

Chapter 9 deals with the analysis of the $\text{Se}_{1-x}\text{Te}_x\text{As}_{10}$ alloys, which form an intricate two-phase structure upon crystallization. The alloy was thermally analyzed similarly to the SeTe alloy in chapter 7. We also report a novel method developed to transfer samples from UFDSC to TEM, which allows microstructural analysis. We show that the combination of both methods is a powerful tool for structural and thermal analyses.

When a chapter has been published in a peer-reviewed journal, this is mentioned on the first page of the chapter. A full list of publications can be found at the end of this thesis.

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